Stable isotopes and organic geochemistry in peat: Tools to investigate past hydrology, temperature and biogeochemistry

ERIN L. MCCLYMONT1, E. PENDALL2 AND J. NICHOLS3
1School of Geography, Politics and Sociology, Newcastle University, UK; erin.mcclymont@ncl.ac.uk
2Department of Botany and Program in Ecology, University of Wyoming, USA; 3NASA Goddard Institute for Space Studies, New York, USA

Characterizing the stable isotope and biomarker geochemistry of peat cores enables reconstruction of key climatic and environmental variables in the past, including temperature, hydrology and the cycling of carbon.

Proxy targets and the value of geochemistry

Peatlands are valuable archives of terrestrial environmental change due to their sensitivity to the hydrological regime and the excellent preservation of organic matter. Peat geochemistry reflects the composition of the original peat-forming plant assemblage (which is itself dependent on air temperature and hydrology), and the subsequent transformation of that organic matter in the aerobic surface layer (the acrotelm) and the anaerobic catotelm (below the water table). Changes to air temperatures and water table depth are thus reflected in peat via changes to both organic matter input and its subsequent degradation (Fig. 1). Precipitation and evaporation cause isotopic fractionation of hydrogen (δD) and oxygen (δ18O), so that the isotopic composition of the meteoric water used by peatland plants reflects a combination of precipitation source and peatland hydrology (Daley et al., in press). Stable carbon isotopes (δ13C) give important information on carbon pathways, including fractionation during photosynthesis (White et al., 1994; Williams and Flanagan, 1996), and the recycling of organic matter and consumption of CO2 and methane by microbial activity (Pancost et al., 2000).

Humic acid formation during degradation of plant material (humification) is a proxy for peatland wetness (Yeloff and Mauquoy, 2006). Total carbon and nitrogen contents also indicate wetness (McClymont et al., 2008), since drier conditions cause the plant remains to spend a longer time in the acrotelm, where degradation preferentially releases nitrogen over carbon (Kuhry and Vitt, 1996). However, isolating whether changes to biomass and/or peatland hydrology drive the humification or bulk geochemistry signals recorded in peat cores makes environmental interpretations of such records difficult (Yeloff and Mauquoy, 2006). Here, we discuss the

Perspectives

The comparison of testate amoeba-inferred water table depth, δ18O data from Sphagnum stems, and instrumental climatic data revealed some interesting correlations. We now need 1) more high-resolution multi-proxy studies similar to that from Mauntshas to determine if these patterns can also be observed elsewhere, and 2) manipulative experiments to assess the relative influences of temperature, precipitation and water table depth on testate amoeba communities and the Sphagnum δ18O isotopic signal. Such combined studies will help understand which factors most strongly control the development of alpine peatlands, how these peatlands can be fully exploited for inferring paleoclimatic and environmental signals, and how they may respond to ongoing and future climate changes.

References


Figure 3: Confidence bands (95%) of detrended (upper panel) and non-detrended (lower panel) pollen-based warm-season temperature reconstructions (red) versus measured temperature (solid black line) during the instrumental period. Pollen picked up long-term (at least decadal-scale) temperature changes (e.g., 1900–1950). Time series were detrended to reduce the effects of human impact. Calibration period (AD 1954 onwards) and verification period (pre-AD 1954) are delineated by a dashed vertical line (modified from Kamenik et al. 2009).
potential for organic and stable isotope geochemistry analyses to determine more precisely the climatic and environmental evolution of peatlands (Fig. 1).

**Isotopic analysis of plant remains**

Different peat-forming plants can have distinct chemical characteristics that reflect their different water sources and biochemical pathways (Fig. 1). For example, *Sphagnum* mosses contain higher carbon/nitrogen ratios than vascular plants (Kuhry and Vitt, 1996). The absence of functioning guard cells, which encircle the leaf pores used in gas exchange (stomata) and regulate the size of the stomatal opening, prevents control over water loss and gas exchange (Loader et al., 2007). Thus the isotopic composition of *Sphagnum* cellulose potentially records the isotopic composition of meteoric waters (Pendall et al., 2001). However, a bulk peat sample contains variable contributions from different plant sources, which limits efforts to isolate the controls over the signals recorded. Manually picking the remains of specific plants reduces such errors and yields a cleaner hydrological/climatic signal.

For example, White et al. (1994) exploited the differences in CO₂ uptake between *Sphagnum* and sedges, recorded in their δ¹³Ccellulose to reconstruct Holocene atmospheric CO₂ concentrations, although temperature and humidity effects on δ¹³C had also to be considered. *Sphagnum* δ¹³Ccellulose has also been shown to be strongly related to mean air temperatures along a transect in SW Poland (Skrzypek et al., 2007). However, careful sample selection is required to minimize the impacts of inter- and intra-plant variability in *Sphagnum* δ¹³C (Loader et al., 2007).

A strong temperature signature in the δD of *Sphagnum* tissues in Patagonian peatlands has been paired with humidity reconstructed from δ¹³C in Carex (a sedge genus) fragments to provide a record of Holocene climate change that is independent of vegetation change as recorded in pollen (Pendall et al., 2001). *Sphagnum* cellulose δ¹⁸O from Walton Moss (UK) was dominated by the precipitation δ¹⁸O (Daley et al., in press). Given strong modern temperature controls over δ¹⁸O in the UK and also in Nova Scotia, Daley et al. (2009; in press) used Holocene *Sphagnum* cellulose δ¹⁸O to reconstruct paleotemperatures. However, the influences of evaporation/peatland surface wetness (Daley et al., in press), and changing δ¹⁸O of the precipitation source (Daley et al., 2009) under different climate regimes complicated interpretations. Adoption of multi-proxy...
strategies can help disentangle these various factors.

Development of biomarker proxies

Analyzing manually picked plant remains requires good preservation, which is not always characteristic of well-humified peats. Alternatively, organic geochemistry techniques can characterize bulk samples of peat, in cases where specific molecules or groups of compounds (biomarkers) are associated with particular peat-forming plants, microbial activity, or diagenetic transformations. Two principal methods have been employed in peats (Fig. 2): analysis of solvent-extractable lipids, and analysis of biomacromolecules via thermal degradation techniques (pyrolysis).

Compounds that are specific to particular peat-forming plants (Fig. 2) include the 5-n-alkylresorcinols (in sedges; Aavsej et al., 2002), a group of triterpenoids, the taraxeroids (in Ericaceae rootlets; Pancost et al., 2002), and a pyrolysis product of sphagnum acid, 4-isopropenylphenol (Boon et al., 1986; van der Heijden et al., 1997). The most widely applied markers for peat-forming plants are the straight chain hydrocarbons from plant waxes, the n-alkanes, whose dominant chain-lengths differ between Sphagnum (usually C29, C30) and non-Sphagnum (>C24) species (Baas et al., 2000; Bingham et al., 2009; Nichols et al., 2006; Nott et al., 2000). These relationships and the post-depositional stability of the n-alkanes have enabled changing plant inputs to be detected (Fig. 3) (McClymont et al., 2008; Nott et al., 2000). Compound-specific stable isotope analysis also allows simultaneous generation of isotopic information for both Sphagnum and non-Sphagnum species.

Mechanisms of organic matter degradation have been determined and linked to Holocene water table depths because microbial activity and chemical transformations are controlled by oxygen and hydrogen availability. Biomarker records of degradation include the stereochemical transformations of hopanes and the presence of anaerobic and aerobic microbial lipids in Holocene peats (McClymont et al., 2008; Pancost et al., 2003). Methanogenesis (formation of methane by microbes) in peats has been identified by the presence and δ13C signature of lipids derived from Archaea (Pancost et al., 2000). A pronounced increase in archaeal lipid concentration in the catotelm of Swedish peat supported this interpretation, and could potentially be used to assess water table depth (Weijers et al., 2004). The preferential degradation of plant macromolecules (e.g., polysaccharides, lignin) under aerobic and anaerobic conditions can also be detected (Schellekens et al., 2009). Applying these relationships down-core may offer insights into both changing water table depth and the biogeochemical response to such events.

Application of compound-specific isotope analysis

Ombrotrophic peatlands contain two distinct plant groups that potentially draw water from different reservoirs and are distinguishable by different leaf wax biomarkers (Fig. 1). Sphagnum uses water from within water-retaining (hyaline) cells and that held among the leaves and branches, which may be strongly affected by evaporation and therefore enriched in deuterium (D) relative to precipitation. In contrast, vascular plants use water from below the surface in the acrotelm, protected from evaporation and representative of precipitation δD (Nichols et al., 2009). Further fractionation during biosynthesis leads to vascular plant cellulose being systematically enriched relative to Sphagnum, and this is also reflected in n-alkane δD (Menot-Combes et al., 2002). By measuring δD of both vascular plant (peatland water before evaporation) and Sphagnum biomarkers (peatland water after evaporation), and assuming that vascular biomarkers were not affected by evapotranspiration, Nichols et al. (2010) calculated Holocene evaporation in north America. This approach has also enabled both peatland wetness and precipitation seasonality to be determined in Holocene peats from Norway, and subsequently linked to the sea-surface temperatures in the Norwegian Sea (Nichols et al., 2009) (Fig. 3).

Two major factors affect δ13C of Sphagnum biomarkers: Sphagnum water content and the amount of recycled methane contributing to the CO2 pool used by Sphagnum for photosynthesis. When Sphagnum is more saturated, the water film over the photosynthetic cells impedes the incorporation of CO2, and thus the plant becomes less selective against 13C.

Figure 3: Biomarker records from a peatland on the Lofoten Islands of arctic Norway (modified from Nichols et al., 2009). A) Norwegian Sea Surface Temperature (SST) on reverse scale, plotted for regional context (Calvo et al., 2002). B) δD of precipitation derived from δD of the vascular plant biomarker, nonacosane. From ~9 ka to 6 ka, warm SSTs allowed for increased winter precipitation at the coastal Norway site, resulting in depleted annual average δD of precipitation. C) The Sphagnum/Vascular ratio is an n-alkane biomarker ratio indicating the relative contribution of Sphagnum and vascular plants to the peat. The contribution of Sphagnum to the peat declines rapidly with the decrease in summer precipitation at 9 ka. Sphagnum recover at 6 ka, but not fully, indicating the region is drier during this period. D) δδ is the fraction of water remaining in Sphagnum after evaporation, based on the comparison of the δD of Sphagnum and vascular plant biomarkers. In this Norwegian peatland, evaporation increases as the region becomes cooler and drier.
Peat cellulose isotopes as indicators of Asian monsoon variability

Bing Hong1, M. Uchida2, X.T. Leng3 and Y.T. Hong1

1State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Beijing, China; hongbing@vip.skleg.cn
2Environmental Chemistry Division, National Institute for Environmental Studies, Tsukuba, Japan; 3Institute of Peatmire, Northeast Normal University, Changchun, China

Stable isotopes in peat cellulose provide records of Asian monsoon variability in the Holocene and suggest persistent teleconnections between the Asian monsoons and North Atlantic climate variability.

Peat cellulose isotopes as proxy climate indicators

A practical proxy for climate reconstruction for the Holocene epoch should be able to span about 10 ka with decadal to centennial time resolution. Over the last 20 years oxygen and carbon isotope analysis of peat cellulose has been developed as a Holocene palaeoclimate proxy (Brenninkmeijer et al., 1982; Hong et al., 2000, 2001; Ménot-Combes et al., 2002). Peat plant cellulose is a macromolecular polymer of interlinked dextroglucose molecules (Hong et al., 2009; and see McLaymont et al., this issue), formed from oxygen atoms derived from the water used by the plant and carbon atoms derived from atmospheric CO2. The stable isotopic composition of cellulose oxygen and carbon is influenced by different physical and chemical processes. Oxygen isotopes (δ18O) in water molecules undergo temperature-dependent fractionation during condensation. Variations in δ18O of meteoric water are generally positively correlated with atmospheric temperature (Dansgaard, 1964). During photosynthesis, the δ13C signature of the source water is recorded in cellulose molecules. Source water for photosynthesis in many peatlands is primarily meteoric, although it may be enriched by evaporation. Vascular plants respond to variations in water availability and relative humidity by regulating the opening or closing of leaf stomata. This leads to changes in the stable carbon isotopic composition (δ13C) of atmospheric CO2 utilized in photosynthesis (Franey and Farquhar, 1982; Schleser, 1995). The amount of rainfall is also negatively correlated to the plant δ13C value; the larger the amount of rainfall, the smaller the δ13C value (Lee et al., 2005; Wang et al., 2008). Therefore, information on climatic changes is preserved in the δ18O and δ13C values of peat plant cellulose. Finally, plant cellulose is highly resistant to decomposition. Both cellulose and its isotopes are highly stable over periods of approximately 105 years (Briggs et al., 2000). Peat plant cellulose isotopes therefore have significant potential as a bioindicator of palaeoclimatic changes. Here we summarize the contribution of peat cellulose isotopes to the reconstruction of East Asian monsoon variability during the Holocene.

Spatial variation of the EASM and peatland distribution

Recent advances in extraction and purification of cellulose from bulk peat samples have allowed application of peat cellulose isotopes (Hong et al., 2000, 2001) to reconstruct the history of the Asian summer monsoon (e.g., Hong et al., 2009). Peat deposits of northern China are largely dominated by sedges, so the isotopic sig-

References


For full references please consult:
http://www.pages-igbp.org/products/newsletters/ref2010_1.html